

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 081 282
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 82305052.1

(51) Int. Cl.³: C 03 B 37/025

(22) Date of filing: 24.09.82

(30) Priority: 15.10.81 US 311786

(43) Date of publication of application:
15.06.83 Bulletin 83/24(84) Designated Contracting States:
AT BE DE FR GB IT NL(71) Applicant: Corning Glass Works
Houghton Park
Corning, New York, 14831(US)(72) Inventor: Miller, Stephen Bruce
67 West Fourth Street
Corning New York 14830(US)(72) Inventor: Schultz, Peter Charles
9475 Scott Road
Painted Post New York(US)(74) Representative: Kyle, Diana et al,
ELKINGTON AND FIFE High Holborn House 52/54 High
Holborn
London WC1V 6SH(GB)

(54) Low temperature method and apparatus for making optical fibers.

(57) A glass optical waveguide preform is formed by chemical reaction of gaseous and/or vapourised ingredients (A and B) within a glass substrate tube (52). A reactant feed tube (50) extends into a first end of the substrate tube (52). One of the reactants (A) flows through the feed tube (50), and another (B) flows through the annular channel between the feed (50) and substrate (52) tubes. The reactants (A and B) combine just downstream of the end of the feed tube (54) and react to form particulate material, of which at least a portion is deposited on the substrate tube (52). The output end of the feed tube (50) traverses (58, 60) the substrate tube (52) so that the region of maximum soot deposition moves along the length of the substrate tube. A hot zone (54, 56) traverses (18a', 18b') the substrate tube (52) in synchrony (58) with the feed tube (50) to sinter the deposited soot.

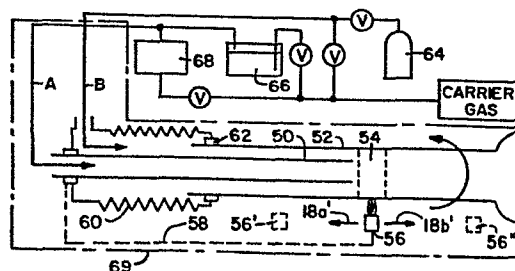


Fig. 3

EP 0 081 282 A1

LOW TEMPERATURE METHOD AND APPARATUS
FOR MAKING OPTICAL FIBERS

This invention relates to a low temperature method and apparatus for making optical fibers, and more particularly to such a method and apparatus which are useful in the manufacture of low loss optical wave-
5 guide fibres capable of propagating energy in the infrared region of the spectrum.

The overloaded condition of communication systems in the 1960's motivated a search for higher capacity transmission media. Although glass optical fibers were
10 known, their attenuation was too high for use in such systems. Improved processing techniques such as that disclosed in U.S. Patent No. 3,711,262 have resulted in optical waveguide fibers having attenuation levels sufficiently low that they are now widely used in
15 telecommunication systems. Such progress has been made in silica-based fibers that fibers of this type have been produced having attenuations less than 0.5 dB/km at 1.55 μm . It has been reported that the ultimate loss for silica glass fibers might be 0.18
20 dB/km, which is limited by intrinsic loss due to infrared absorption bands and Rayleigh scattering.

In order to achieve even lower loss transmission, materials capable of transmission in the infrared region of the spectrum are being investigated. The publication,
25 J.R. Gannon, "Optical Fiber Materials for Operating Wavelengths Longer Than 2 μm ", Journal of Non-Crystalline Solids, vol. 42 (1980), pp. 239-246, sets forth calculated attenuation minima for a number of potential materials.

It is speculated that ZnCl_2 and BeF_2 should achieve attenuation minima of 0.001 dB/km at 3.7 and 2.1 μm , respectively.

U.S. Patent No. 4,188,089 teaches a chemical
5 vapour deposition (CVD) technique for forming fibers
having light-conducting regions formed of selected
non-oxide compositions. A carrier gas such as
chlorine or any other halogen or an inert gas such as
He, Ar, or Kr entrains vapours of the reactant gases.
10 All such vapours are premixed and delivered to the end
of a substrate tube through which they flow unreacted
until they reach the moving hot zone. Upon reaching the
region of elevated temperature, a reaction takes place
which causes a vitreous layer to be deposited within the
15 substrate tube. This layer is composed predominantly of
anions S, Se and/or Te. Cations are Ge, Si, P, B, As,
Sb and/or Ti. The light transmitting core of the
resulting optical waveguide fiber cannot include certain
elements such as beryllium, zinc, aluminium and lead
20 which do not form volatile halides.

Fluoride glass fibers formed by a conventional
rod drawing technique are disclosed in the publication,
S. Mitachi et al., "Fluoride Glass Fiber for Infrared
Transmission", Japanese Journal of Applied Physics,
25 Vol. 19, No. 6, June, 1980, pp. L313-L314. Mixtures
of GdF_3 , BaF_2 and ZrF_4 were melted at 800°C in a gold
crucible, and glass rods were prepared by pouring
the melts into brass moulds. The glass rods were
drawn into fibers by a conventional fiber fabrication
30 technique. Losses as low as 480 dB/km were measured
at 3.39 μm for fibers several meters long.

U.S. Patent No. 4,189,208 teaches a method of
forming an optical fiber having a core of ZnCl_2 by
drawing the fiber from a melt. Because of the
35 impurities which are introduced into the fiber by

forming it in this manner, this technique has not been capable of providing fibers having losses as low as those which are formed by vapour deposition techniques.

U.S. Patent No. 3,722,981 teaches a method of
5 drawing low-melting fluoride glasses from a melt. Although it is estimated that the Rayleigh scattering loss of such fibers is about 1 dB/km, the impurity absorption losses of fibers formed by this technique are unacceptably high. It is stated in the publication
10 Y, Ohishi et al., "Impurity Absorption Loss due to Rare Earth Elements in a Fluoride Glass", Japanese Journal of Applied Physics, vol. 20, No. 3, March, 1981, pp. L191-L193, that rare earth impurity concentration in fluoride optical fibers should be decreased to
15 less than 0.1 ppbw in order to make the absorption loss 0.001 dB/km in the 3-4 μ m wavelength range.

We have therefore sought to provide a method and apparatus for forming by a vapour deposition process optical waveguide fibers which are suitable
20 for transmitting energy in the infrared region of the spectrum.

We have further sought to provide a method and apparatus for delivering highly reactive reactants to the deposition region of a substrate tube.

25 Thus, the present invention relates to a method and apparatus for manufacturing a preform which is intended to be subsequently drawn into an optical filament. This method is of the type that includes the steps of flowing vapours of at least two glass-
30 forming reactants into a hollow, cylindrical glass substrate. The vapour mixture is reacted within the substrate to produce particulate material which travels downstream where at least a portion thereof comes to rest on the inner surface of the substrate where it is
35 fused to form a continuous glassy deposit on the inner

surface of the substrate. The improvement of the present invention comprises maintaining the reactants separate until they reach the region of the substrate wherein the reaction product is produced.

5 In a preferred embodiment, the apparatus of the present invention comprises tubular means for maintaining one reactant separate from another reactant, at least one of the reactants flowing from the tubular means into the substrate tube. This apparatus is especially
10 appropriate for producing by exothermic reaction in the substrate tube particulate material which deposits and is consolidated to form a layer of metal halide glass. Vaporous or volatile sources which provide the cation and anion of the resulting metal halide glass must be
15 employed. The cationic vapour source is a compound containing the cation of the product glass which bears an organometallic substituent or other anionic substituent which renders the compound into a volatile state. The anionic vapour source is a halogenating
20 agent.

The invention is illustrated with reference to the accompanying drawings wherein:-

Figure 1 is a schematic representation of a prior art apparatus for depositing a glass layer within a
25 tube;

Figure 2 shows a section of the tube of Figure 1 depicting observed conditions during processing;

Figure 3 is a schematic representation of an apparatus suitable for practice of the deposition process
30 in accordance with the present invention;

Figure 4 is a cross-sectional view of the apparatus of the present invention depicting conditions occurring during processing;

Figures 5 and 6 show alternative arrangements for
35 feeding reactants into a substrate tube;

Figure 7 shows a cross-sectional view of a substrate tube in which glass layers have been deposited;

5 Figure 8 shows a cross-sectional view of the substrate tube after it has been collapsed;

Figure 9 is a graph illustrating the refractive index profile of an optical fiber produced in accordance with one embodiment of this invention;

10 Figures 10 and 11 illustrate alternative embodiments whereby particulate material can be deposited to form a preform; and

Figure 12 shows a particulate material generator that can be employed in the apparatus of Figures 10 and 11.

15 Figures 1 and 2 show a prior art system comprising a substrate tube 10 having a handle tube 8 affixed to the upstream end thereof and exhaust tube 12 affixed to the downstream end thereof. Tubes 8 and 12 are chucked in a conventional glass-turning lathe (not
20 shown), and the combination is rotated as indicated by the arrow. The handle tube, which may be omitted, is an inexpensive glass tube having the same diameter as the substrate tube, and it does not form a part of the resulting optical waveguide. A hot
25 zone 14 is caused to traverse tube 10 by moving heating means 16 as schematically depicted by arrows 18a and 18b. Heating means 16 can consist of any suitable source of heat such as a plurality of burners encircling tube 10.

30 Reactants are introduced into tube 10 via inlet tube 20, which is connected to a plurality of sources of gases and vapours. Flow control valves are represented by a circle having the letter "V" therein. A source 22 of carrier gas is connected by valves 26 and
35 28 to reservoirs 32 and 34, respectively. The carrier

gas may be any gas which is compatible with the reactants and with the reaction taking place in tube 10, such as oxygen, chlorine, helium, argon, nitrogen and krypton. Reservoirs 32 and 34 usually contain
5 normally liquid reactant materials which are introduced into tube 10 by bubbling the carrier gas therethrough. Gaseous source 36 is connected by valve 30 to inlet tube 20. Exiting material is exhausted through exhaust tube 12.. Not shown is an arrangement of mixing valves,
10 shutoff valves and system controller which may be utilized to meter flows and to make other necessary adjustments in composition.

Burner 16 initially moves at a low rate of speed relative to tube 10 in the direction of arrow 18b, the
15 same direction as the reactant flow. Although the reactants are premixed, they do not react until they reach the hot zone 14. The reaction produces a powdery suspension of particulate material, often referred to as "soot", which is carried downstream to region
20 42 of tube 10 by moving gas. As burner 16 moves in the direction of arrow 18b, hot zone 14 moves downstream so that a part of soot buildup 44 extends into the hot zone and is consolidated thereby to form a unitary, homogeneous glassy layer 48.

25 When the burner 16 reaches the end of the tube 10 adjacent to the exhaust tube 12, the temperature of the flame is reduced and the burner returns at a faster rate in the direction of arrow 18a to the input end of the tube 10. Thereafter, additional layers of
30 glassy material are deposited within tube 10 in the manner just described. After suitable layers have been deposited to serve as the cladding, barrier layer and/or core material of the resulting optical waveguide

fiber, the temperature of the glass is increased to cause the tube to collapse. This can be accomplished by reducing the rate of traverse of the hot zone.

5 In the deposition of oxide glasses, which are typically doped silicas, both the oxidation of the metal halide vapours and the sintering of the oxide soot only occur at an appreciable rate at temperatures above 1200°C. As a result, pure silica or a high silica content glass substrate tube is required to
10 contain the process without becoming badly deformed. A consequence of the use of a refractory tube, however, is the need for even higher temperatures in the range of 1900°C and above to accomplish the tube collapse and fiber draw steps.

15 The need for high temperature in all phases of this prior art process results in several disadvantages. The refractory glass substrate tubes which are required in this process are costly and are difficult to manufacture with close geometric tolerances and high glass quality.
20 The furnaces capable of achieving 2000°C for the fibre drawing step are generally expensive, difficult to control, and have relatively short refractory muffle/heating element life-times. In general, this high temperature process is costly from an energy consumption
25 standpoint and requires complex equipment and procedures.

In accordance with the present invention at least two reactants, referred to herein as reactant A and reactant B, are kept separated until they reach the desired reaction zone in the substrate tube. Each
30 of reactants A and B comprises one or more compounds which do not react detrimentally among themselves. However, when reactants A and B are mixed, they begin spontaneously to react at ambient temperature to form a metal halide glass material in particulate form and
35 gaseous by-products. As shown in Figure 3, reactant A

flows through a tube 50 which is situated on the axis of substrate tube 52. Reactant B is fed into substrate tube 52 and flows through the annular channel formed between tubes 50 and 52. In the illustrated embodiment the reaction zone where reactants A and B are combined is the hot zone 54 created by heat source 56. Thus, that portion of tube 50 within substrate tube 52 terminates just prior to the hot zone. Even though the reaction may be exothermic and require little or no heat for complete reaction to occur, heat source 56 should be employed for the purpose of consolidating the deposit of particulate material on the inner surface of tube 52. Burner 56 would not be needed if one or only a few layers of particulate material were deposited and were not consolidated until a later time such as during the fiber drawing operation. If the heat source were located along the length of tube 50, as illustrated at 56', it would preheat at least some of the reactant vapours as well as consolidate particulate matter as it moved in direction 18b'. Burner location 56' would be undesirable for certain reactants which would be adversely affected by the heat. If the burner were located at position 56", it would have to be located downstream from the reaction zone a distance sufficiently great to ensure that the thermophoresis effect would not be negated. Location 56" may be the most desirable burner position for a process which utilized a reactant that would be adversely affected by the heat generated thereby.

The reactant vapours may be obtained from various types of sources. Illustrated in Figure 3 are gaseous source 64, liquid source 66 and solid source 68. Source 68 may be the type taught in U.S. Patent No. 3,801,294. Reactants such as $\text{Be}(\text{CH}_3)_2$, which must

be maintained at an elevated temperature to generate sufficient vapour pressure, must be transported through lines that are maintained at an elevated temperature to prevent condensation in the lines.

5 If such a material is being employed, the appropriate delivery lines and the substrate tube can be situated in an oven represented by broken line 69. Also, delivery lines can be insulated or heated to prevent condensation.

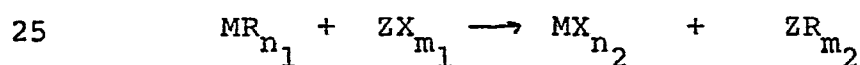
10 Tube 50 could be replaced by two or more tubes, each of which deliver reactants to the reaction zone. Such tubes could be coaxial as illustrated in Figure 5 or side-by-side as illustrated in Figure 6. All of the reactant vapours could travel through the inner
15 tubes, as indicated by arrows A and B of Figures 5 and 6. One of the reactants could travel in the region between the inner tubes and outer tube 52' as indicated by arrow C of Figures 5 and 6. If three or more separated reactants are required, they could be supplied
20 to the reaction zone through three or more coaxial tubes or three or more side-by-side tubes.

Referring to Figure 3, tube 50 is mechanically coupled by means represented by dashed line 58 to burner 56 to ensure that the tube 50 is continuously
25 maintained the proper fixed distance from burner 56. Alternatively, the heat source and the tube 50 may be kept stationary, and the rotating substrate tube may be traversed. The input end of the tube 52 is connected to tube 50 by a collapsible member 60,
20 a rotating seal 62 being disposed between member 60 and tube 52. Tubes 50 and 52 could also be interconnected by other types of seals which are known in the art. For example, a cap can be situated over the end of tube 52. Tube 50 passes through an
35 aperture in the cap. A rotary seal is disposed

between tube 50 and the cap.

As shown in Figure 4, reactant vapour A emanating from tube 50 reacts with reactant vapour B flowing in the direction of the arrows between tubes 50 and 52, thereby generating particulate material 63 which flows downstream where at least a portion thereof deposits on the wall of tube 52 as shown at 44'.

The apparatus of Figures 3 and 4 is especially appropriate for producing by exothermic reaction in a substrate tube particulate material which forms a metal halide glass. For such reaction to occur within the substrate tube requires the employment of vaporous or volatile sources for the cation and anion of the resulting glassy product. The cationic vapour source is a compound which contains the cation of the product halide glass and bears an organometallic substituent or substituents or other anionic substituent or substituents which renders the compound into a volatile state. The anionic vapour source is a halogenating agent, i.e. a compound having halide substituents which become the anion of the product halide glass. A general equation for such reaction is:



where in the cationic vapour source:

M = the cation of the desired resulting halide glass,

R = the anion substituent of the cationic, i.e. the organometallic or other substituent which renders compound, MR_{n_1} into a volatile state,

n_1 = the number of substituents required for electrical neutrality,

and in the halogenating agent:

Z = the cation,

X = the halide of the halogenating agent which
is to become the halide of the product metal

5 halide glass and,

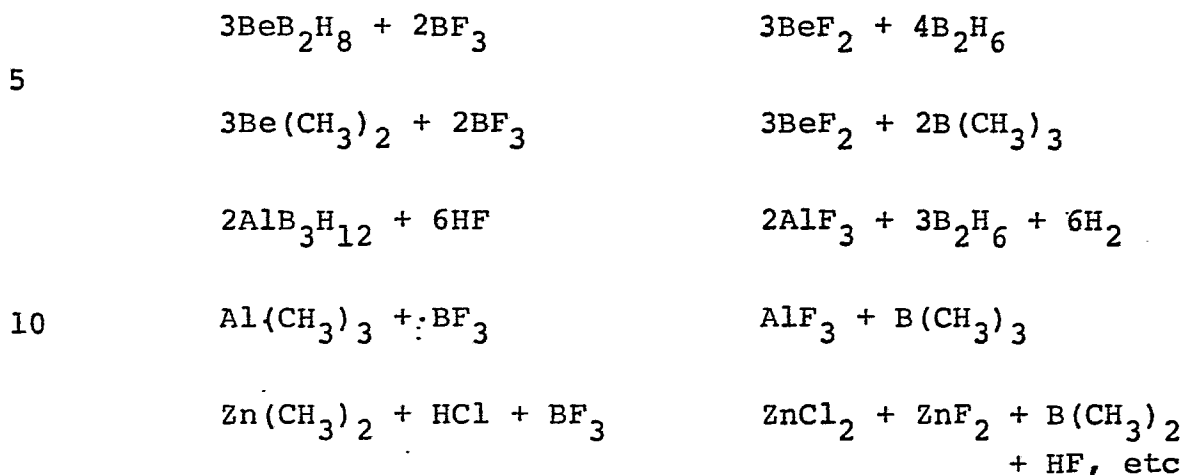
m_1 = the number of halides required for electrical
neutrality.

The compound MX_{n_2} is the resulting metal halide glass,
and ZR_{m_2} is a gaseous byproduct. In some reactions
10 there may be a plurality of different cationic and/or
anionic sources. Examples of cationic vapour sources
are organometallic compounds, borohydrides and β -
diketonés.

Certain organometallic compounds, especially
15 those possessing alkyl substituents, are frequently
the only materials which will render a particular
cation into a volatile state suitable for reaction.
Organometallic compounds vary widely in their reactivity
owing primarily to the electronic distribution
20 around the central cation. Whereas organometallic
compounds of silicon such as tetramethylsilane
(CH_3)₄Si are volatile, air and moisture stable,
highly combustible materials, other compounds such
as trimethylaluminium $Al(CH_3)_3$, dimethylzinc
25 $Zn(CH_3)_2$, and dimethylberyllium $Be(CH_3)_2$ are
electron deficient and are therefore pyrophoric
when exposed to air and react vigorously with oxygen
and water. Similarly, the highly reactive
organometallic compounds undergo numerous reactions
30 with other electron-donating reagents.

Of particular interest for use in the present
invention are those reactions which produce the metal
halide from gaseous halogenating agents such as
 BF_3 , SiF_4 , COF_2 , HF, HCl, $SiCl_4$, BCl_3 and the like.
35 Following are some exemplary metathesis reactions
whereby gaseous and/or vaporous reactants may be

delivered to the reaction zone to form solid metal halide glass materials and gaseous reaction by-products:



Obviously, the above list is intended to be exemplary of the numerous reactions which may be employed to obtain a metal halide glass in accordance with the present invention. The latter listed equation, which is not stoichiometrically balanced, represents a reaction whereby the combination of ZnCl_2 and ZnF_2 is formed. This optical glass material is described in Japanese Patent Application Disclosure 56-2265 entitled "Glass Material for Optical Glass Fiber", N. Mitaji et al., filed August 3, 1979.

Although gaseous HF would probably yield the cleanest reaction chemistry, its presence may not be compatible within a SiO_2 -based glass tube. Milder fluorinating agents are much safer to use in the formation of fluoride glasses. Compounds of the other halogens are also of interest in the present method in order to form chloride, bromide or iodide glasses. If reactions of the type forming B_2H_6 are to be employed, care should be taken due to the dangerous nature of the resulting compounds.

Vapours of the halogenating agent are preferably introduced between the interior walls of tube 52 and the

-13-

the exterior wall of the axially located tube 50. Vapours of the cationic vapour source would be supplied via the inner tube 50. In this manner a vaporous cationic source, especially certain organometallic compounds which would be detrimentally affected by excess heat, would be transported to the reaction zone along a path which is spaced from the hot substrate tube wall. If the vaporous cationic source is not detrimentally affected by excess heat, it could be transported as described above, or it could be transported in the annular region between tubes 50 and 52, the halogenating agent then flowing through tube 50. The reaction will commence as soon as the two streams come into contact. The particulate material then flows downstream where at least a portion thereof deposits on the wall of tube 52 in a conventional manner to form buildup 44'. While the exact shape of the region 63 of particulate material formation and flow is not known and the exact shape of deposit 44' is not known, these two regions have been illustrated in Figure 4 in accordance with the generally accepted theory of thermophoresis force whereby particulate material is forced toward the centre of a tube in the region of a burner and thereafter flows from the hot stream toward the cooler wall section of the tube downstream from the burner. A layer 48' of sintered particulate material is formed in the region heated by the external burner. Since the entire process can be conducted in a dry, clean environment and since the products themselves are expected to be of high purity, it should be possible to deposit multiple layers of pure, optical quality, hydroxyl-free metal halide core glass.

Some perceived advantages of the approach of the present invention are as follows. It should be possible

to form very high purity homogeneous fluoride glass. Contaminants such as 3d, 4d and 5d transition element, rare earths and hydroxyl ions should be virtually eliminated by distillation of the metal alkyls, and by drying the starting gases. Nucleation sites for crystallization, for example, dirt are eliminated. Even though toxic, non-durable glasses, such as fluoride glasses, may be employed as the core material, fiber toxicity and durability problems are minimized, since the outer cladding of the fiber is a durable, non-toxic glass. Only the fiber ends expose the fluoride glass to the environment. In typical applications the ends are hermetically sealed in splicing and coupling devices. This minimizes the risk of exposure to personnel and should greatly enhance strength characteristics. Moreover, because of the low temperatures at which reactions can be carried out and sintering and drawing can be performed, the aforementioned disadvantages of high temperature operations can be eliminated.

Both single mode and multi mode optical waveguide fibers can be made by this technique. Because of the glasses which can be formed in accordance with the present invention, extremely low loss optical fibers for propagation in the infrared region of the spectrum can be theoretically fabricated. Since it is contemplated that the light conducting region of the optical fibers may comprise such elements as beryllium and zinc, these fibers may exhibit improved resistance to ionizing radiation since these elements have slightly higher ionization potentials than silicon.

The following examples illustrate the manner in which optical waveguide fibers having metal halide glass cores can be made by low temperature deposition and drawing processes.

Example 1

A commercially available alkali borosilicate glass substrate tube 52 (Corning Code 7073) having a thermal coefficient of expansion (TCE) of about $53 \times 10^{-7}/^{\circ}\text{C}$ is mounted and rotated in a glass-working lathe. A reactant tube 50 of refractory material such as silica, alumina, platinum or the like is mounted in the substrate tube in the manner described hereinabove. Reservoir 64 contains BF_3 , while reservoirs 68 and 66 contain $\text{Be}(\text{CH}_3)_2$ and $\text{Al}(\text{CH}_3)_3$, respectively. Reservoir 66 is a conventional bubbler, and reservoir 68 is a vapour generator of the type taught in U.S. Patent No. 3,801,294. Since the vapours from reservoir 68 condense if not maintained at a temperature of about 170°C the feed line from reservoir 68 and the entire lathe assembly are situated in oven 69 which is maintained at 190°C . As shown in Figure 7 a barrier cladding layer 70 is initially formed on the inner surface of tube 52 by flowing reactants from reservoirs 64 and 68 into tubes 52 and 50, respectively. There is no flow at this time from reservoir 66. The reaction produces pure BeF_2 soot which deposits on the inner surface of tube 52 and is sintered to form layer 70. The refractive index n_D of this layer is about 1.28 and the TCE thereof is about $67 \times 10^{-7}/^{\circ}\text{C}$. The sintering temperature, i.e., the temperature generated at the inner surface of tube 52 by burner 56, can be approximately 500°C . After a layer of sufficient thickness has been deposited, the flow of reactants from reservoirs 64 and 68 is continued, and in addition, reactant vapours are flowed from reservoir 66 in an amount necessary to form a core glass layer, the composition of which is 7.5 mole percent AlF_3 and 92.5 mole percent BeF_2 . After a layer of sufficient thickness has been deposited,

the tube 50 is extracted, and then the temperature of the resultant tubular member is increased to approximately 800°C, thereby causing the tube to collapse to form a blank having the cross-section illustrated in Figure 8, wherein layers corresponding to those of Figure 7 are represented by primed reference numerals. The collapsing step can be performed by traversing the burner at a low speed along the rotating tube 52. During this operation the temperature within the oven 69 should be maintained at about 500°C, the annealing temperature of tube 52, to avoid thermally-induced stresses which would otherwise cause tube breakage. A multimode fiber could be drawn from this blank at a temperature in the range of 800°C. Since the refractive index n_D of the core layer 72 is about 1.31, the NA of the resultant fiber should be about 0.28. The refractive index profile of the resulting fiber is illustrated in Figure 9. Since the refractive index of the core layer and the barrier/clad layer are less than that of the substrate tube, the barrier/clad layer must be sufficiently thick to permit it to function as the cladding of the resulting optical waveguide fiber.

Example 2

A single mode fiber is formed in accordance with Example 1 except for the following modifications. The flow rates of $\text{Be}(\text{CH}_3)_2$ and $\text{Al}(\text{CH}_3)_3$ are adjusted to form a core of 1 mole percent AlF_3 and 99 mole percent BeF_2 , the cladding layer again comprising pure BeF_2 . The core and barrier/cladding layers are deposited in such thicknesses that in the resulting fiber the core diameter is 10 μm , and the vapour deposited barrier cladding thickness is 30 μm while the substrate tube outer cladding thickness is 27.5 μm . The core refractive index n_D is 1.285. Thus,

the NA is about 0.11, and the cutoff wavelength is 800nm.

Example 3

A soda-lime silicate glass tube, such as Corning Code 0080 glass, having a TCE of about $100 \times 10^{-7}/^{\circ}\text{C}$ is employed as the substrate tube. Reservoir 64 contains BF_3 , and reservoirs 66 and 68 contain $\text{Pb}(\text{CH}_3)_4$ and $\text{Al}(\text{CH}_3)_3$, respectively. Both of reservoirs 66 and 68 are bubblers since the reactants disposed therein are liquids. To form the barrier clad layer, the flow of reactants from reservoirs 66 and 68 is controlled such that, when these reactants react with BF_3 a barrier clad layer having a composition of 50 mole percent PbF_2 and 50 mole percent AlF_3 is formed. Thereafter, the flow of vapours from reservoirs 66 and 68 is modified so that a core layer having a composition of 70 mole percent PbF_2 and 30 mole percent AlF_3 . The average TCE of the deposited core and cladding glasses is about $130 \times 10^{-7}/^{\circ}\text{C}$. The sintering step can be performed at a temperature of about 500°C . The tube collapse temperature and fiber draw temperature should be about 700°C . Since the reactive indices of the core and barrier clad glasses are about 1.71 and 1.66, respectively, the NA of the resultant fiber should be about 0.5.

Example 4

This example sets forth a method which could be employed to form a fiber having a predominantly ZnCl_2 core. A glass comprising ZnCl_2 and BiCl_3 could be employed as the core layer since the refractive index thereof is higher than that of ZnCl_2 , which is about 1.7. Since the TCE of ZnCl_2 is about $280 \times 10^{-7}/^{\circ}\text{C}$, a high expansion substrate tube should be employed. A suitable glass for this purpose is one having the composition, 30 mole percent SnF_2 , 34 mole percent SnO , 3 mole

percent PbF_2 and 30 mole percent P_2O_5 , which has an expansion coefficient of about $270 \times 10^{-7}/^\circ\text{C}$. This fluorophosphate glass is described in U.S. Patent No. 4,314,031 entitled, "Tin-Phosphorous Oxyfluoride Glasses" filed June 17, 1980 in the name of C.M. Sanford et al. Reservoir 64 would contain HCl and reservoirs 66 and 68 would contain $\text{Zn}(\text{C}_2\text{H}_5)_2$ and $\text{Bi}(\text{CH}_3)_3$, respectively. Since all of these reactant sources are liquids, reservoirs 64, 66 and 68 are bubblers or other suitable containers for liquids. A barrier clad layer could be formed by flowing suitable amounts of vapours from reservoirs 64 and 66. The sintering temperature would be approximately 175°C . After a barrier clad layer of sufficient thickness is deposited, the flow of vapours from reservoir 68 is initiated, and the vapours from reservoirs 64, 66 and 68 would react to form the ZnCl_2 - BiCl_3 core layer. The tube collapse temperature and the fiber draw temperature is about 275°C .

Whereas the above description and examples have been specifically directed to the deposition of glass layers on the inner surface of a substrate tube, it is not intended that the present invention be limited to such an apparatus and method. Indeed, it is also applicable to the outside vapour deposition (OVD) technique and the axial vapour deposition (AVD) technique, for example. Examples of the OVD technique are disclosed in U.S. Patents Nos 3,737,292 and 3,823,995. Examples of AVD techniques are taught in U.S. Patents Nos 3,957,474; 4,062,665; 4,224,046 and 4,231,774.

Figure 10 illustrates an apparatus which can be employed to form an optical fiber preform by an OVD technique. A mandrel 78 rotates and translates

back and forth in a vessel 80 as illustrated by the arrows. Dry inert gas such as Ar, N and He is fed into vessel 80 through conduit 81 and is exhausted therefrom through conduit 82. The inert gas ensures a dry,
5 oxygen-free atmosphere within the vessel. A generator 83 directs a stream 84 of particulate material toward mandrel 78 where a deposit is formed. Flameless heating means such as resistance heater 86 increases the temperature of the deposit so that particulate
10 material 84 impinging upon the deposit will adhere thereto. The resulting porous preform 85 can be pulled from mandrel 78 and then consolidated in either vessel 80 or an attached environmental chamber. Thereafter, the consolidated blank can be drawn into an optical
15 fiber in a conventional manner.

Particulate generator 83 can be a simple coaxial vapour feed source of the type illustrated in Figure 11. It could simply consist of concentric tubes 89 and 90. Reactants A and B described above
20 could be fed into tubes 89 and 90, respectively. When the two reactants combine at the output end of the tubes, they spontaneously react to form a stream of particulate material.

In the embodiment of Figure 12 a vessel 91 is
25 supplied with dry, inert gas through conduit 92, the gas being exhausted through conduit 93 along with any gaseous by-products which are formed in vessel 91 during formation of metal halide particulate material. A mandrel 94 rotates and translates upward as indicated
30 by the arrows. The mandrel has an enlarged end portion on which a preform 95 is formed by axial deposition of particulate material from generator 96. As the length of preform 95 increases, the mandrel moves away from generator 96 to maintain a constant distance
35 between the preform and generator 96. Thermal energy

may be supplied by a resistance heater 97 for the purpose of causing the particles to adhere to the preform or for causing the particles actually to sinter and form a preform of consolidated glass.

- 5 A layer of cladding material can be deposited on the initially formed portion of the preform by utilizing one or more additional particulate material generators 98. Another resistance heater 99, may be employed to cause the deposited particulate material
- 10 from generator 98 either to adhere to the preform or to be completely consolidated thereon.

CLAIMS

1. A method of forming an optical fiber comprising forming glass precursor particulate material by reacting at least two reactants in a reaction zone to form a suspension of particulate reaction product, depositing
5 the particulate reaction product on a substrate to yield an optical fiber preform, and drawing the optical fiber preform into an optical fiber, characterized in that the at least two reactants are maintained separate until they reach the reaction zone adjacent to the substrate.
- 10 2. A method according to claim 1, wherein the reaction product is a metal halide, one of the glass-forming reactants being a compound containing a cation of the resulting metal halide and an anionic substituent which renders the compound into a volatile state, another
15 of the reactants comprising a halogenating agent.
3. A method according to claim 2 wherein one of the said reactants is an organometallic compound.
4. A method according to claim 2, wherein the method includes the step of fusing the deposit of particulate
20 material while the particulate reaction product is being deposited to form a continuous glassy deposit.
5. A method of manufacturing an optical device, which includes the step of flowing vapours of at least two glass-forming reactants into a hollow, cylindrical glass
25 substrate where they react to form a suspension of particulate reaction product material which travels downstream where at least a portion thereof comes to rest on the inner surface of said substrate to form a deposit thereon, characterised in that the at least
30 two reactants are maintained separate until they reach the region of the substrate wherein the reaction product is produced.
6. A method according to claim 5, wherein the step

of flowing comprises introducing tubular means into the substrate, one of the reactants flowing through the tubular means.

7. A method according to claim 5, wherein the
5 reaction product is a metal halide, one of the glass-forming reactants being a compound containing a cation of the resulting metal halide and an anionic substituent which renders the compound into a volatile state, another of the reactants comprising a halogenating agent.
- 10 8. A method according to claim 7, wherein one of the reactants is an organometallic compound.
9. A method according to claim 7, wherein the method includes the step of fusing the deposit of
15 particulate material to form a continuous glassy deposit on the inner surface of the substrate, the method further comprising the step of heating the substrate to a temperature sufficiently high to close the aperture therein, thereby forming a preform.
10. A method according to claim 9, further comprising
20 the steps of heating the preform to the drawing temperature of the materials thereof and drawing the preform to form an optical waveguide fiber.
11. A method according to claim 7, further comprising the step of heating the substrate to the drawing temperature thereof and drawing the preform while simultaneously
25 fusing the deposit of particulate material and closing the aperture within the substrate to form an optical waveguide fiber.
12. A method of manufacturing an optical waveguide
30 preform which includes the steps of flowing into a first tube at least two reactants which react to form particulate material, at least a portion of which form a deposit on the inner surface of the first tube, and moving a heat source along the outside of the first tube
35 to sinter the deposit of particulate material and form

a glass layer, the improvement which comprises moving tubular means within the first tube while maintaining the end of the tubular means, which is within the first tube, in fixed spaced relation to the heat source, and
5 passing one of the reactants through the tubular means, whereby the reactants remain separated until they become mixed downstream from the end of the tubular means.

13. A method of manufacturing an optical waveguide
10 fiber preform, the method including the steps of flowing vapours of at least two glass-forming reactants into a reaction zone within a hollow cylindrical glass substrate to form metal halide particulate material, at least a portion of which comes to rest on the inner
15 surface of the substrate to form a deposit thereon, and moving the reaction zone along the length of the substrate, characterized in that the step of flowing comprises flowing through a first path vapours of a first compound which comprises a cation of the metal
20 halide and an anionic substituent of the cation which renders the compound into a volatile state, and flowing through a second first path vapours of a halogenating agent.

14. An apparatus for manufacturing from a hollow,
25 cylindrical substrate a preform which is intended to be subsequently drawn into an optical fiber, the apparatus comprising means for rotatably supporting the substrate, means for introducing into a reaction zone in the substrate a vapour mixture including at least two glass-
30 forming reactants, the vapour mixture being capable of reacting within the substrate to form a suspension of particulate material which travels downstream where at least a portion thereof comes to rest to form a deposit on the inner surface of the substrate, the improvement
35 comprising means for preventing the mixing of the two reactants until they reach the reaction zone.

15. An apparatus according to claim 14, wherein the apparatus further comprises means for heating an axial section of the substrate so that the temperature is substantially uniform around a circumferential section thereto, thereby forming a hot zone within the substrate, and means for moving the heating means longitudinally with respect to the substrate, the means for preventing comprising tubular means situated within the substrate for delivering at least one of said reactants to the reaction zone.

16. An apparatus according to claim 15, further comprising means for maintaining a fixed distance between the heating means and the end of the tubular means which is situated within the substrate.

17. An apparatus according to claim 16, wherein the tubular means comprises a tube disposed in the first end of the cylindrical substrate, an end of the tube terminating within the substrate, one of the reactants flowing through the tube into the reaction zone, and the other of the reactants flowing to the reaction zone through the annular channel between the tube and the substrate.

18. An apparatus according to claim 16, wherein the tubular means comprises at least two concentric tubes disposed in the first end of the cylindrical substrate, the ends of the tubes terminating within the substrate, one of the reactants flowing through the centrally located tube into the reaction zone, and the other of the reactants flowing to the reaction zone through the annular channel between the centrally located tube and the tube surrounding the centrally located tube.

19. An apparatus according to claim 16 wherein the tubular means comprises at least two tubes disposed side-by-side in the first end of the cylindrical substrate an end of each of the tubes terminating within the substrate, one of the reactants flowing through a first of the tubes into the reaction zone, and the other

0081282

-25-

of the reactants flowing to the reaction zone through another of the tubes.

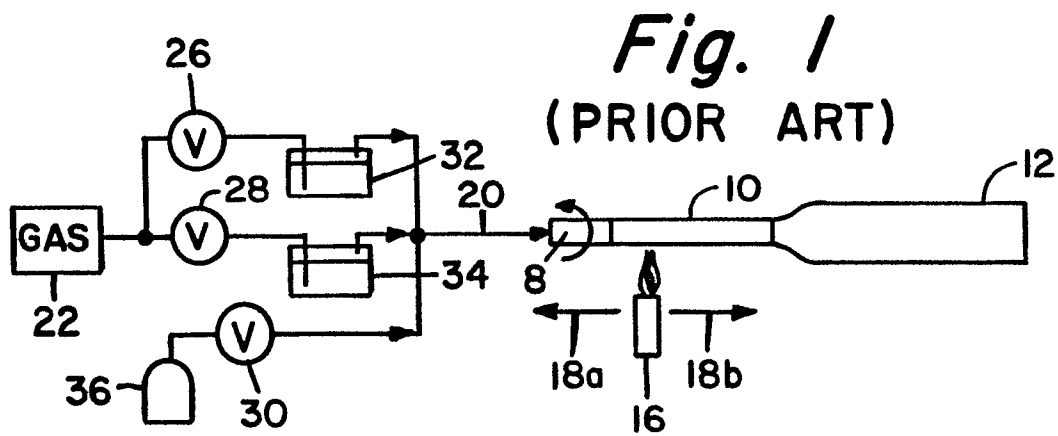
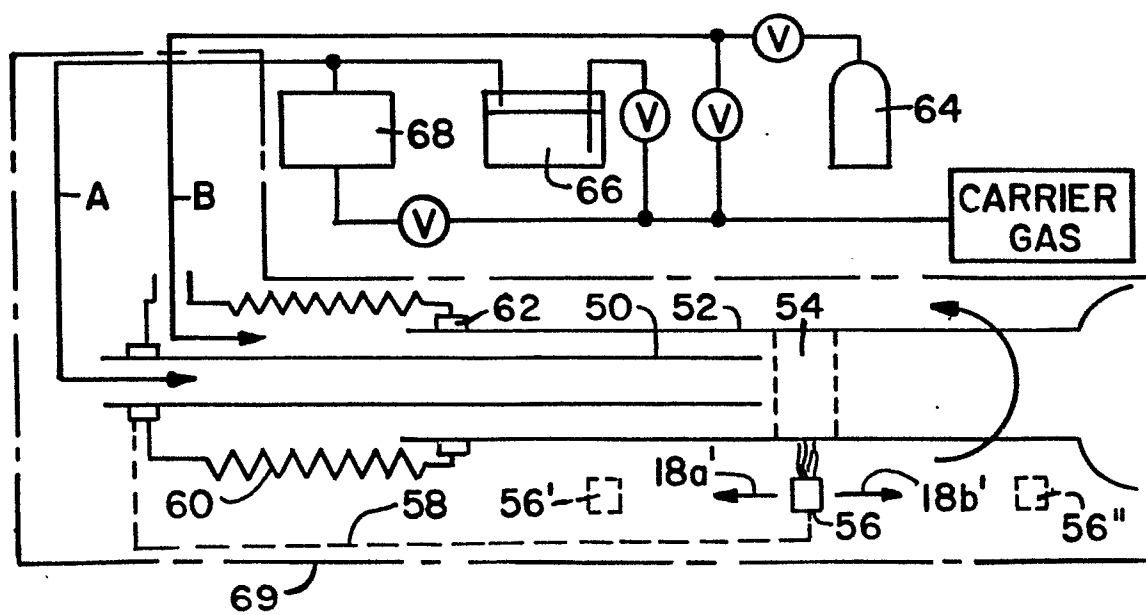
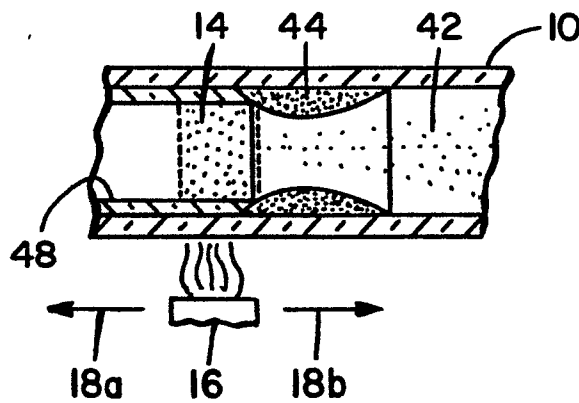
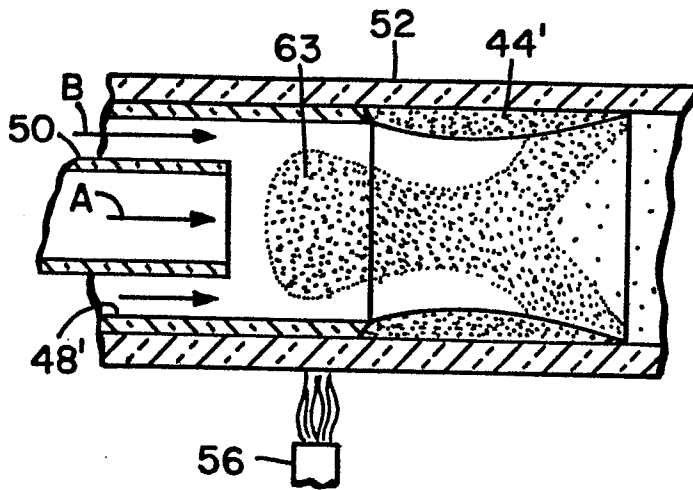
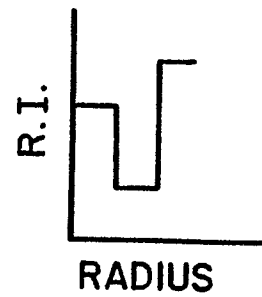
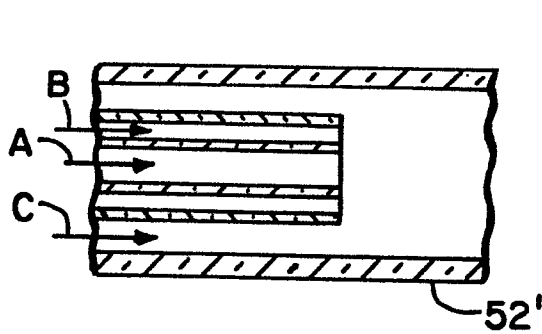
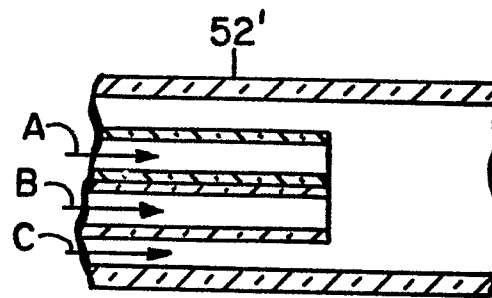
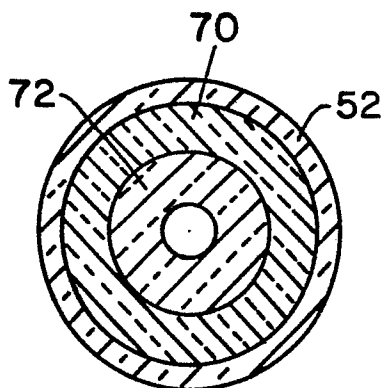
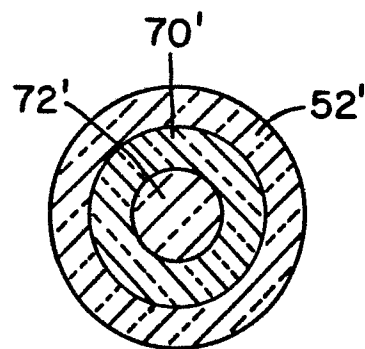
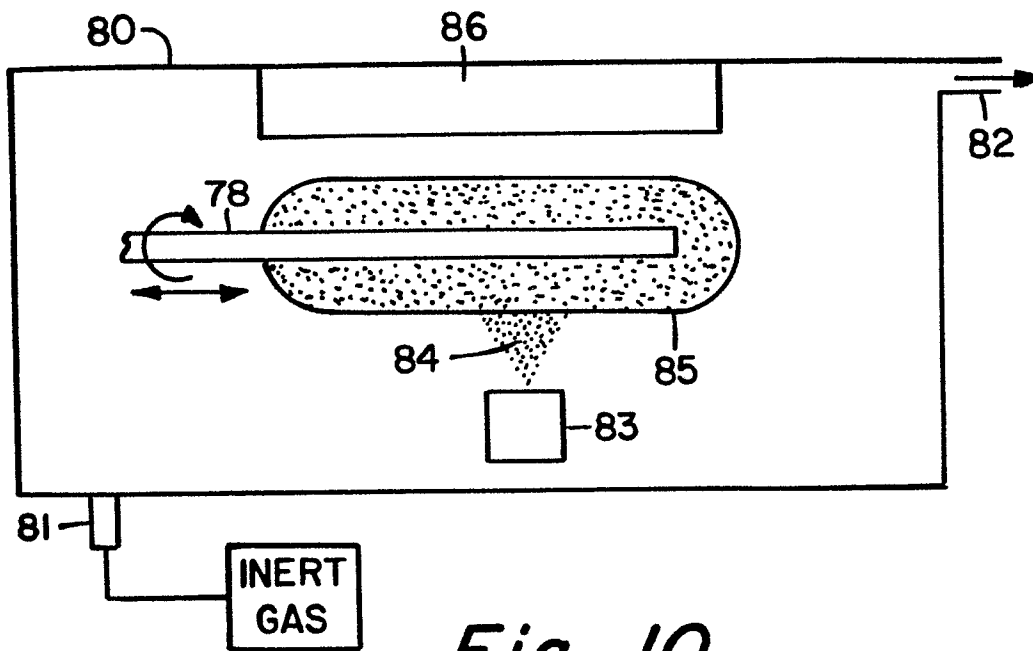
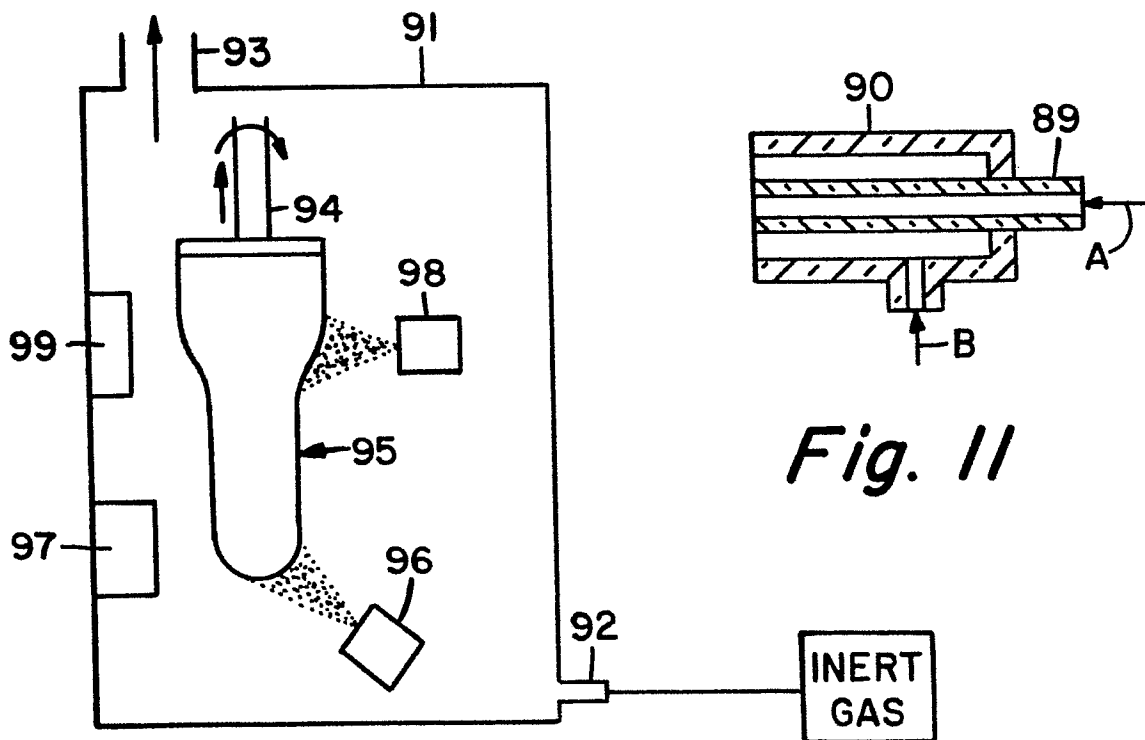


Fig. 2
(PRIOR ART)



*Fig. 4**Fig. 9**Fig. 5**Fig. 6**Fig. 7**Fig. 8*

*Fig. 10**Fig. 11**Fig. 12*



European Patent
Office

EUROPEAN SEARCH REPORT

0081282

Application number

EP 82 30 5052

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	--- GB-A-2 023 129 (CORNING GLASS WORKS) * claims 1, 6; figures 3, 4 *		C 03 B 37/025
A	--- US-A-4 263 032 (W.R. SINCLAIR et al.) * figure 8 * -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 03 B 37/025
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 07-01-1983	Examiner STROUD J.G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			